

GAS-PHASE COMBUSTION SYNTHESIS OF NONOXIDE NANOPARTICLES IN MICROGRAVITY

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INTRODUCTION

Gas-phase combustion synthesis is a promising process for creating nanoparticles for the growing nanostructure materials industry. The challenges that must be addressed are controlling particle size, preventing hard agglomerates, maintaining purity, and, if nonoxides are synthesized, protecting the particles from oxidation and/or hydrolysis during post-processing. Sodium-halide Flame Encapsulation (SFE) is a unique methodology for producing nonoxide nanoparticles that addresses these challenges [1,2]. This flame synthesis process incorporates sodium and metal-halide chemistry, resulting in nanoparticles that are encapsulated in salt during the early stages of their growth in the flame (Fig. 1). Salt encapsulation has been shown to allow control of particle size and morphology, while serving as an effective protective coating for preserving the purity of the core particles. Metals and compounds that have been produced using this technology include Al, W, Ti, TiB₂, AlN, and composites of W-Ti and Al-AlN [2,3]. Oxygen content in SFE synthesized nano-AlN has been measured by neutron activation analysis to be as low as 0.54wt.% [4], as compared to over 5wt.% for unprotected AlN of comparable size [5].

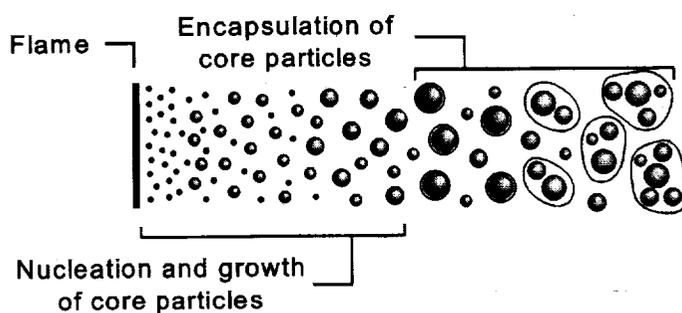


Fig. 1 - Schematic of Particle Encapsulation

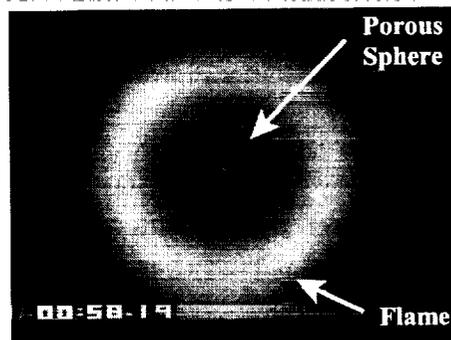


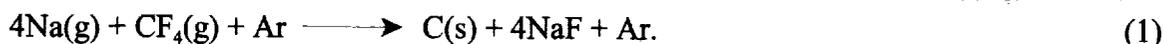
Fig.2 - Sodium-Halide Flame in μg

The overall objective of this work is to study the SFE process and nano-encapsulation so that they can be used to produce novel and superior materials. SFE experiments in microgravity allow the study of flame and particle dynamics without the influence of buoyancy forces. Spherical sodium-halide flames (Fig. 2) are produced in microgravity by ejecting the halide from a spherical porous burner into a quiescent atmosphere of sodium vapor and argon. Experiments are performed in the 2.2 sec Drop Tower at the NASA-Glenn Research Center. Numerical models of the flame and particle dynamics were developed and are compared with the experimental results.

EXPERIMENT SETUP

The metal halide chosen for the microgravity experiments was carbontetrafluoride (CF₄). CF₄ is an attractive precursor because it is nonhazardous and exists as a gas at standard conditions, unlike many of the metal-halides used to produce the materials previously mentioned. Furthermore,

the characteristics of the encapsulation process are not a strong function of the choice of metal-halide. Therefore, information gained from studying synthesis and encapsulation of carbon can be applied to the synthesis of other materials. An additional reason for using CF_4 is that nano-carbon particles are not reactive in air. Since particles will be extracted from the flames and examined by electron microscopy to determine their morphology, it is important that unencapsulated core particles be nonreactive. Nanometer-sized metal and nonoxide ceramic particles would react rapidly when exposed to air. The reaction for the production of carbon is given by



A stainless-steel combustion chamber was constructed for the drop tower experiments (Fig. 3). To maintain sufficient sodium vapor concentration, the chamber walls are heated to temperatures ranging from 600 to 700 °C using resistive heat tapes. Sodium is stored in a reservoir located near the base of the chamber. By keeping the top surface of the chamber slightly cooler than the rest of the chamber, sodium condenses on the top surface during charging, and a saturation condition is achieved. The partial pressure of sodium in the chamber is then known from vapor pressure data. Argon is added to achieve the desired sodium concentrations and the chamber is operated at subatmospheric pressure.

The halide/argon mixture is delivered to the chamber through a 1/4" spherical porous stainless-steel burner with a pore size of 10 micron. The chamber is equipped with two access ports, both of which can be used as windows for video recording. A pneumatic piston-actuating assembly may also be installed at the top port for particle sampling or temperature probing.

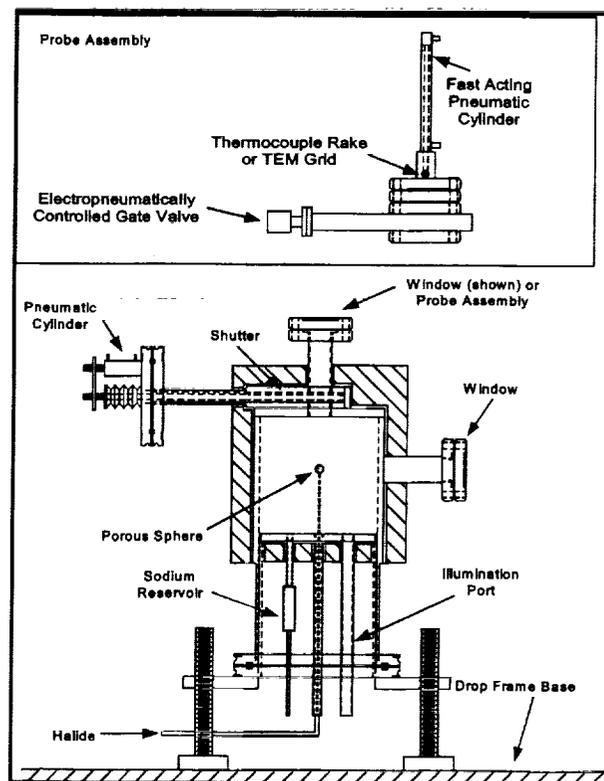


Fig. 3 - Microgravity Combustion Chamber Schematic

RESULTS

Figure 4 shows a series of images of a sodium-halide flame during a 2.2 second drop. The flame was produced with an initial sodium mole fraction of 0.33. The CF_4 /argon mixture was 20% CF_4 by volume, and was delivered through the porous sphere at a rate of 32.9 mg/min.

The sodium-halide reaction is hypergolic. Therefore, no ignition source is required, but controlling the exact time of ignition is challenging because the time for delivery of the halide varies with run conditions. The flame in Fig. 4 was ignited in 1g, and dropped immediately after visual evidence of ignition.

There are significant differences between the characteristics of flames that are obtained in microgravity and those produced in 1g. In normal gravity, a blueish flame with a much narrower

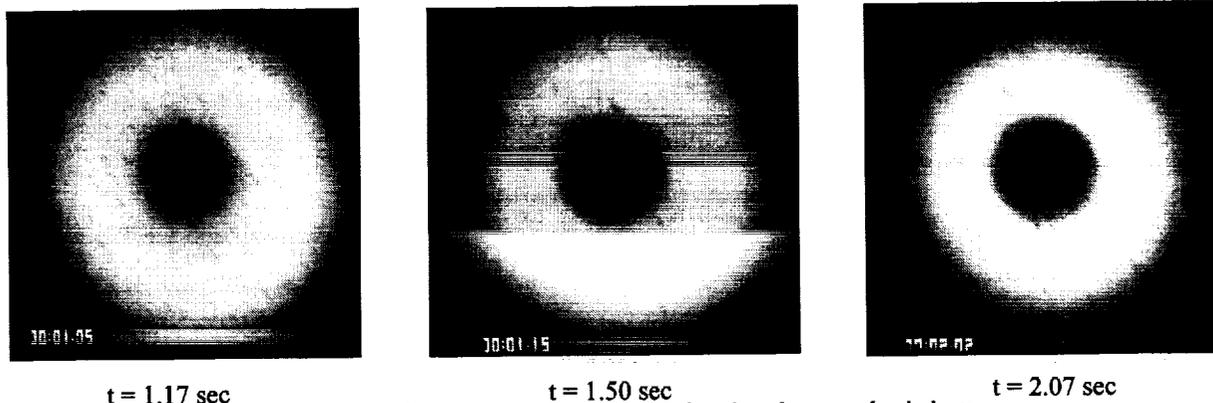


Fig. 4 - Video-frame sequence of encapsulated-carbon synthesis in μg

flame thickness was produced. For chamber pressures in the range of 300-500 mmHg, microgravity flames were too dim to easily distinguish from the background, and appeared to grow much larger than their 1g counterparts. Enhanced mixing due to buoyant flows in normal gravity reduces flame size and increases flame intensity. Indeed, the flame in Fig. 4 transformed to a smaller, thin blue flame immediately after impact at the bottom of the tower.

The video of the flame shown in Fig. 4 clearly revealed the existence of a uniformly dispersed field of large particles (on the order of 1 mm) emitting from the flame. After performing a series of runs in microgravity, which included this case, a sample of the large particles that had impacted on the base of the chamber was collected. A scanning electron micrograph of the surface of this sample reveals a monodisperse distribution of spherical NaF particles (Fig. 5a). The characteristic size of these salt particles is $1.9 \mu\text{m}$ (Fig. 5b). In this sample there is no evidence of unencapsulated carbon particles. This is consistent with results from laminar and turbulent jet flames [1,3,4] in which the core particles were found to be encapsulated in salt, and it implies that the carbon particles in the sample are indeed embedded in the salt spheres.

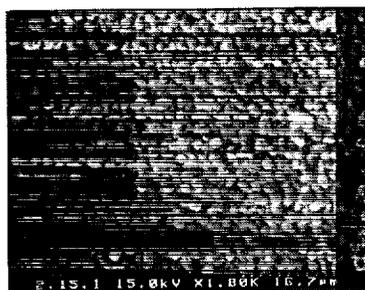


Fig. 5a - Monodisperse distribution of NaF particles

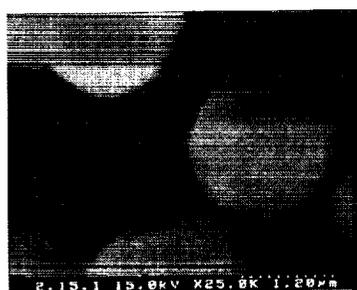


Fig. 5b - Typical NaF sphere

NUMERICAL MODELING

A numerical code was developed to model a 1-D spherical diffusion flame in the absence of buoyancy. This program employs the SANDIA packages for evaluating kinetics and gas-phase thermal and mass transport properties [6]. The code uses a two-point boundary value solver to solve the partial differential equations by the modified Newton-Raphson iteration method [7]. The flame in Fig. 4 was modeled with this program. At steady state, the model predicted a flame radius of 0.74 cm (Fig. 6). This is consistent with the region of the bright zone shown in Fig. 4, where the total radius in the last frame is approximately 0.85 cm. The flame code predicted a maximum flame

temperature of 2023 K.

A numerical multi-component aerosol model employing a Monte Carlo simulation (MCS) has been developed under this program [8]. Thus far the model has only been applied to a homogenous closed system. However, the qualitative results for salt condensation and encapsulation are relevant to this study. The salt is initially in the vapor phase, and the simulation shows that the core particles that are produced in the flame initially grow as they do in a typical flame aerosol. However, as the temperature drops, the salt begins to condense on particles in the tail of the size distribution. The Kelvin effect keeps salt from condensing on all but the largest core particles. The heterogenous condensation of salt rapidly leads to large salt particles having a narrow size distribution. These large salt particles then scavenge the remaining core particles. The experimental results represented in Fig. 5a support this description of the aerosol evolution. In the future, the MCS will be incorporated into the 1-D flame code in order to study nano-encapsulation within the flame.

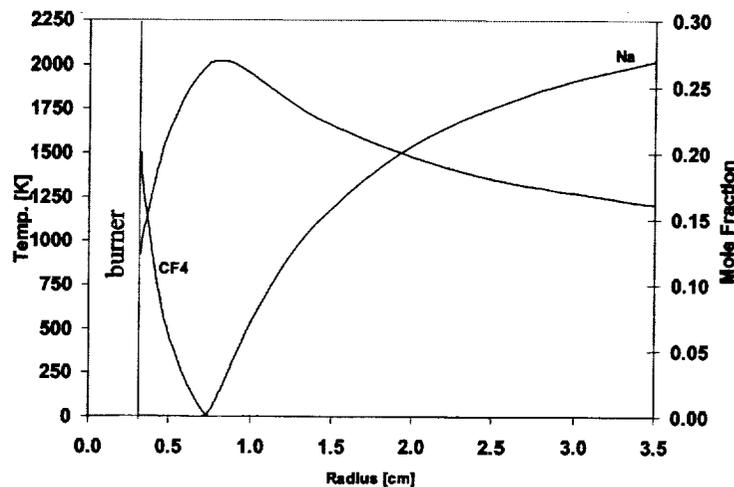


Fig. 6 - Results from 1-D flame code, $m = 32.9$ mg/min

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